AD-A198 244

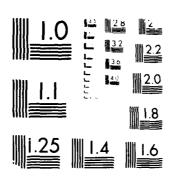
ALKALI METAL DIFFUSE BAND LASERS(U) IOMA UMIU IOMA CITY 1/1

UNCLASSIFIED

AFOSR-84-8178

F/G 9/3

ML



MICROCOPY RESOLUTION 1E-1 CHART

REPORT D	OCUMENTATION PAGE	
AD-A190 244	16. RESTRICTIVE MARKINGS None	
	3 DISTRIBUTION AVAILABILITY OF REPORT	
26 DECLASSIFICATION, DOWNGRADING SCHEDULE	Unclassified/Unlimited	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) IADBL/3	5. MONITORING ORGANIZATION REPORT NUMBER(S) 7 3 6	
6a. NAME OF PERFORMING ORGANIZATION  University of Iowa  (If application)		
6c. ADDRESS (City, State, and ZIP Code)  Iowa City, IA 52242	76 ADDRESS (Crty, State, and ZIP Code) Bolling Air Force Base, D.C.	
Ba. NAME OF FUNDING/SPONSORING ORGANIZATION (If applicable A. F. Office of Scientific Res		
Sc. ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS	
Bolling Air Force Base, D.C.	PROGRAM PROJECT TASK WORK UNIT ACCESSION NO.	
Alkali Metal Diffuse Band Lasers (Unclassified)  12 PERSONAL AUTHOR(S)  ELECTER		
William C. Stwalley  13a TYPE OF REPORT Final Technical Report FROM 6/1/86 TO 5/31/87  14 DATE OF REPORT (Year, Month, Day) August 12, 1987  16 SUPPLEMENTARY NOTATION		
	FERMS (Continue on reverse if necessary and identify by block number)  MER, LASERS, SINGLE —	
19 ABSTRACT (Continue on reverse if necessary and identify by block number)		
on diffuse bands of the alkali metal va of sodium vapor and the yellow diffuse tailed modeling of single vibrational-r overlapping singlet and triplet "excime The gain and low absorption loss previous optical pumping of sodium vapor and pot tively examined. Prospects for laser os where quenching is not dominant. Free- triplet portion of the diffuse bands) he tassium, rubidium and cesium.	a new class of potential excimer lasers based apors. In particular, the violet diffuse bands bands of potassium vapor have been shown by detotational level emission to be each composed of er" emission continua of the diatomic molecule. Susly found in the violet and yellow with laser assium vapor, respectively, have been quantitateillation appear to be good at low pressures bound-free spectra (which include only the lave been produced and analyzed in sodium, po-	
WI UNCLASSIFIED/UNLIMITED SAME AS RPT DTIC USERS Unclassified/Unlimited		
NAME OF RESPONSIBLE INDIVIDUAL  (K) HOWHILD K, KNIOS PERCO  (XII) 762-4900  (XII) 762-4900		

Final Technical Report

for

Air Force Office of Scientific Research grant

AFOSR-84-0178, "Alkali Metal Diffuse Band Lasers"

for

June 1, 1986-May 31, 1987

William C. Stwalley Principal Investigator
Professor of Chemistry and Physics and
Director of the Iowa Laser Facility
University of Iowa, Iowa City, Iowa 52242-1294

(319) 335-1299

Accession For

NTIS GRA&I
DTIC TAB
Unannounced
Justification

Ry
Listeft tion/
Aveilability to 3

A.u.U. 500/6
Dist Special

1

## 1. Abstract

Progress is described on study of a new class of potential excimer lasers based on diffuse bands of the alkali metal vapors. In particular, the violet diffuse bands of sodium vapor and the yellow diffuse bands of potassium vapor have been shown by detailed modeling of single vibrational-rotational level emission to be each composed of overlapping singlet and triplet "excimer" emission continua of the diatomic molecule. The gain and low absorption loss previously found in the violet and yellow with laser optical pumping of sodium vapor and potassium vapor, respectively, have been quantitatively examined. Prospects for laser oscillation appear to be good at low pressures where quenching is not dominant. Free-bound-free spectra (which include only the triplet portion of the diffuse bands) have been produced and analyzed in sodium, potassium, rubidium and cesium.

# 2. Research Objectives

The objectives of this project are as follows:

- a. To observe diffuse band emission spectra in alkali metal vapors.
- b. To analyze these spectra in terms of the relevant potential energy curves and transition moments.
- c. To construct new excimer (bound-free) lasers based on these spectra.
- d. To assist Physical Sciences, Inc. (Andover, Massachusetts) in their attempted demonstration of a near infrared solar-pumped sodium vapor laser.

The progress in each of these areas is described below in Sections 3. a., b., c. and d., respectively.

## 3. Research Progress

a. Observation of diffuse band emission spectra in alkali metal vapors

Partly because of the optics and ionization problems in strong UV pumping

of sodium vapor, we have spent more time on the visible-laser-pumped heavier

alkali metals (especially potassium) than originally anticipated.

In particular, the triplet portions of the alkali vapor diffuse bands (in Na, K, Rb and Cs) have been directly excited for the first time (free  $\rightarrow$  bound absorption followed by bound  $\rightarrow$  free emission). A letter (4. 1.) and full paper (4. b.) describing this new technique for isolating the triplet emission have been submitted; the Ph.D. thesis of W. T. Luh presents most of the basic experimental results. Some new previously unobserved lithium diffuse bands in the violet have been found (papers 4. d., e.) using a variety of different excitation wavelengths.

## b. Analysis of diffuse band spectra

The major items of progress in this area were the unequivocal establishment of the correct electronic assignments of the violet bands of sodium vapor (publications 4. a. and f.) and the yellow bands of potassium vapor (publications 4 b., c.). In particular, by exciting single vibrational-rotational levels of the  $2^1\Sigma_u^+$  state and the  $2^3\Pi_g$  state of Na<sub>2</sub> and K<sub>2</sub> we have established that the violet bands of sodium vapor and the yellow bands of potassium vapor are in fact overlapping singlet and triplet bands. The detailed assignments for Na<sub>2</sub> are  $2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  (peaking near 452 nm) and  $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$  (peaking near 436 nm). Thus the variability of the ratio between the 436 nm and 452 nm emission peaks (for both of which we have previously shown there is significant gain) is now understood for the first time. The assignments in potassium include overlapping singlet and triplet emissions ( $2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ , peaking near 570 nm;  $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$ , peaking near 575 nm).

Detailed modeling of free-bound-free spectra has been carried out for the first time for the potassium  $2^3\Pi_g=1^3\Sigma_u^+$  case. Preliminary results (see publication 4. j.) report encouraging but not perfect agreement.

c. Construction of new excimer (bound-free) lasers based on diffuse band spectra.

A "recirculating supersonic molecular beam oven" (RSMBO), was used to provide direct optical access to a thin "sheet" of sodium or potassium vapor for attemped laser oscillation. This oven is now being modified (improved insulation and heating) to allow for high pressure (> 1 torr) operation. The heat pipe trough (developed at Physical Sciences; see d. and paper 4. g.) may also be used in the future. Also we will have available beginning in August a 4.5 kW 10 cm long mercury lamp and power supply (primary use: pump-ing a 60 watt cw alexandrite laser, the second of its kind, custom built by Allied Corporation). We plan to attempt lamp optical pumping with this equipment once laser optical pumping is successful.

An additional interesting possibility is chemical pumping; J. L. Gole (Georgia Tech) has seen strong violet and near ultraviolet chemiluminescence in sodium-halogen reactions which appears to correlate well with our calculations of Na<sub>2</sub>  $2^1\Sigma_{\bf u}^+ \to {\bf X}^1\Sigma_{\bf g}^+$  "violet band" emission (the ultraviolet features are bound-bound transitions). We have sent him copies of our detailed radiative transition probabilities, which he finds give reasonable agreement with his spectra, assuming vibrationally hot Na<sub>2</sub>  $2^1\Sigma_{\bf u}^+$  molecules.

d. Assistance to Physical Sciences, Inc. (Andover, Massachusetts) in their attempted demonstration of a near infrared solar-pumped sodium vapor laser

We have consulted extensively with Physical Sciences, Inc. concerning their solar-pumped near infrared sodium vapor concept, both by phone and visits. We have assisted in the modified design of their heat pipe trough, in their consideration of the kinetics of the active medium, in their laser

fluorescence temperature measurements and by providing values for the absolute bound-bound and bound-free radiative transition probabilities for all vibrational levels in the  $B^1\Pi_u$  -  $X^1\Sigma_g^+$  bands of Na $_2$  (these bands are critical to the production of a high concentration of Na\*, which is in turn critical to their laser concept).

## 4. List of Written Publications

- a. "Electronic Assignments of the Violet Bands of Sodium", G. Pichler, J. T. Bahns, K. M. Sando, W. C. Stwalley, D. D. Konowalow, L. Li and R. W. Field, Chem. Phys. Letters <u>129</u>, 425 (1986).
- b. "Direct Excitation Studies of the Diffuse Bands of Alkali Metal Dimers", W. T. Luh, J. T. Bahns, A. M. Lyyra, K. M. Sando, P. D. Kleiber and W. C. Stwalley, submitted to J. Chem. Phys.
- c. "Electronic Assignments of the Yellow Bands of Potassium". W. T. Luh, K. M. Sando, K. P. Chakravorty, W. C. Stwalley, G. Pichler and D. D. Konowalow, Chem. Phys. Letters <u>131</u>, 335 (1986).
- d. "The 458 nm Diffuse Band of the Lithium Dimer", J. T. Bahns, W. C. Stwalley and G. Pichler, J. Chem. Phys., in press.
- e. "Study of the Shape of the Lithium Diffuse Band by Single and Double Photon Excitation", G. Pichler, J. T. Bahns and W. C. Stwalley in <a href="Spectral Line Shapes">Spectral Line Shapes</a>, Volume 3, edited by F. Rostas (De Gruyter and Co., Berlin, 1985), p. 659.
- f. "Electronic Assignments of the Violet Bands of Sodium", G. Pichler, J. T. Bahns, K. M. Sando, W. C. Stwalley, W. Müller, D. D. Konowalow, L. Li and R. W. Field, in <u>Advances in Laser Science I</u>, edited by W. C. Stwalley and M. Lapp (American Institute of Physics, New York, 1986), p. 160.
- g. "New Heat Pipe Oven Devices for Broad Band Excitation Laser Studies", M. A. DeFaccio, S. J. Davis, D. I. Rosen, W. C. Stwalley and D. O. Ham, in <u>Advances in Laser Science I</u>, edited by W. C. Stwalley and M. Lapp (American Institute of Physics, New York, 1986), p. 165.
- h. "Long Range Potential of the  $A^1\Sigma_u^+$  State of Na<sub>2</sub> using Modulated Gain Spectroscopy", G. Chawla, H. S. Schweda, H. J. Vedder, R. W. Field, S. Churassy, A. M. Lyyra, W. T. Luh and W. C. Stwallev in <u>Advances</u>

- in <u>Laser Science I</u>, edited by W. C. Stwalley and M. Lapp (American Institute of Physics, New York, 1986), p. 466.
- i. "Spectroscopy of Alkali Metal Vapors under Conditions of Interest for Solar Plasma Propulsion", W. C. Stwalley, to appear in Proceedings of the January 1986 University of Dayton/AFOSR Workshop on Solar Plasma Propulsion.
- j. "Free-Bound-Free Resonance Fluorescence in the  $K_2$  Yellow Diffuse Band: Theory and Experiment", W. T. Luh, K. M. Sando, A. M. Lyyra and W. C. Stwalley, submitted to Chem. Phys. Letters.
- k. "Reinvestigation of the  $K_2$  B-X Fluorescence Excited by a Krypton Ion Laser", W. T. Luh, J. T. Bahns and W. C. Stwalley, J. Mol. Spectrosc., in press.
- 1. "Studies of the Diffuse Bands of K<sub>2</sub>, Rb<sub>2</sub> and Cs<sub>2</sub>", W. T. Luh, J. T. Bahns, A. M. Lyyra, K. M. Sando, P. D. Kleiber and W. C. Stwalley, in <u>Advances in Laser Science II</u>, edited by M. Lapp, W. C. Stwalley, and G. Kenney-Wallace (American Institute of Physics, New York, 1987), in press.

- 5. Professional Personnel\* (University of Iowa)
  - a. William C. Stwalley, Principal Investigator
  - b. Paul D. Kleiber, Assistant Research Scientist/Assistant Professor of Physics
  - c. Shawn P. Heneghan, Postdoctoral Research Associate
  - d. Kuo-Kwang Wang, Postdoctoral Research Associate
  - e. A. Marjatta Lyyra, Postdoctoral Research Associate/Assistant
    Research Scientist
  - f. Wei-Tzou Luh, Graduate Student in Physical Chemistry (received Ph.D. in August 1985; passed final exam on thesis entitled "Laser Spectroscopic Studies of Alkali Metal Dimers" on July 5, 1985).
  - g. Steve Evans, Graduate Student in Physical Chemistry
  - h. Juan Figueroa, Graduate Student in Chemical Physics
  - Young-June Cho, Graduate Student in Physical Chemistry (received
     M.S. without thesis in August 1986)
  - j. Vassillis Zafiropulos, Graduate Student in Physical Chemistry
  - k. Warren T. Zemke, Visiting Professor (Summer only)

<sup>+</sup> Copy available on request.

<sup>\*</sup> Other University of Iowa researchers collaborating on this research include Dr. John T. Bahns (Iowa High Technology Council support), Dr. Krishna P. Chakravorty (Visiting Research Scientist with support from the Government of India), and Professor Kenneth M. Sando (unsupported).

## b. Interactions - William C. Stwallev et al

## a. Papers and Seminars

- i. "Diffuse and Interference Bands in Alkali Metal Dimers" Paper ME3 at the 39th Symposium on Molecular Spectroscopy /Columbus Ohio, June 1984).
- ii. "Photophysics and Photochemistry of Alkali Metal Vapors". Department of Physics, University of Missouri (St. Louis, Valv. 1984).
- iii. "Spectra and Potential Energy Curves of Alkali Metal Diatomi-Molecules: Experimental Results Compared with Theory", invited paper at American Chemical Society meeting (Philadelphia, August 1984).
- iv. "Photochemistry and Photophysics of Alkali Metal Vapors", Laser Seminar, University of Toronto (Toronto, October 1984).
- v. "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, Pennsylvania State University (State College, October 1984).
- vi. "Photophysics and Photochemistry of Alkali Metal Vapors", invited paper, International Conference on Applications of Lasers and Electro-Optics (Boston, November 1984).
- vii. "Diffuse Bands in Alkali Metal Vapors" and "Jonization and Energy Transfer in Alkali Metal Vapors", invited papers at Lasers '84 (San Francisco, December 1984).
- viii. "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, University of Michigan (Ann Arbor, January 1985).
  - ix. "Photophysics and Photochemistry of Alkali Metal Vapors", Combustion Research Facility, Sandia National Laboratories (Livermore, February 1985).
  - x. Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, University of Missouri-Rolla (August 1985).
  - xi. "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, Illinois Institute of Technology (September 1985).
- xii. "Electronic Assignments of the Violet Bands of Sodium", "New Heat Pipe Oven Devices for Broad Band Excitation Laser Studies", and "Long Range Potential of the  $A^1\Sigma^+_{\mathbf{u}}$  State of Na<sub>2</sub> Using Modulated Gain Spectroscopy", contributed papers, the first International Laser Science Conference (Dallas, November 1985).

- \*i.. Specifies post Alma C Meta. Vapitus order school of other est for schar Flagta Et 2280 the in ited paper. These of of Last of AF of worest post ocuar Flagta English to Tollage.
- The opening and Profine strong to Aleasi Metal Dapors. In string the of Phisis Perjura Tian in suversity Harbin Instirize of Terminian institute of the balt Lake Wining Lase; institute official large and Past China Domain Supersity April 1886
- Programmes and Photo begistry of Alkali Metal Varons of From the Computer Compute
- (a) I saince temi allo fumiet Alkali Metal Diffuse Band Dasers offichated parer optical Domiets of America Annual Meeting searfile of temocran
- (k): Strines of the Critise Bands of Kj. Ptj. and kg/... officities prove the contributerrational Laser Science Conference of katherine the contributer.
- Schl. "Pr. t prosi o acti frotochemistry it Alkali Metal Vapiss" is partment if Physics Manarisci International University it ter 1966.
  - Six "Photophysis and Photochemistry of Alkal, Metal Vapors", Physics Division - ar Ridge National Laboratory November 1986
  - "Photochemistry and Photophysics of Alkali Metal Vapors" le partment i "hemistry University of Puerto Rico November 1986.
  - xxi "Photochemistry and Photophysics of Alkali Metal Vapors", Lepartment of Chemistry, University of Miami November 1986
- xxii "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, Grinnell College (January 1987).

#### b Consultations

- i. Visited Physical Sciences, Inc. (D. Ham, host) regarding collaboration on solar-pumped near infrared sodium vapor laser (Andover, Massachusetts, July 1984).
- Visited Air Force Weapons Laboratory (S. Davis, host) regarding optically pumped lasers (Albuquerque, New Mexico, October 1984).
- iii. Hosted David Ham, Physical Sciences, Inc., regarding collaboration on solar-pumped near infrared sodium vapor laser (November 1984).

- iv. Visited Physical Science Inc., Andover, Massachusetts (D. Ham, host) regarding collaboration on solar-pumped near infrared sodium vapor laser (Andover, Massachusetts, July and also August 1985).
- v. Visited Howard Schlossberg, AFOSR regarding research progress (May 1986).

## 7. New Discoveries

- a. Discovery of gain at ~565 nm in the yellow bands of potassium vapor.
- b. Discovery that sodium and potassium visible continua represented overlapping singlet and triplet transitions  $(2^1\Sigma_u^+ + X^1\Sigma_g^+)$  and  $(2^3\Pi_g)^+ + (2^3\Sigma_u^+)^+$ , respectively).
- c. Discovery of new violet diffuse bands in lithium vapor.
- d. Discovery of free-bound-free spectra in sodium, potassium, rubidium and cesium vapor which could be described and modeled in terms of  $2^3\Pi_g$   $1^3\Sigma_u^+$  transitions only.

To appear in <u>Advances in Laser Science - II</u>, edited by Marshall Lapp, William C. Stwalley and Geraldine A. Kenney-Wallace (American Institute of Physics, New York, 1987).

Studies of the Diffuse Bands of K2, Rb2 and Cs2

Wei-Tzou Luh\*, John T. Bahns†, Kenneth M. Sando, A. Marjatta Lyyra‡, Paul D. Kleiber‡ and William C. Stwalley‡

Iowa Laser Facility and Department of Chemistry
University of Iowa
Iowa City, Iowa 52242-1294

#### Abstract

Direct dye laser excitations of the  $\rm K_2$  yellow,  $\rm Rb_2$  orange and  $\rm Cs_2$  near infrared diffuse bands have been investigated. Experimental results are shown to be consistent with free-bound  $2^3\Pi_g \leftarrow 1^3\Sigma_u^+$  excitation followed by bound-free emission between the same two states. It is found that for  $\rm Rb_2$  and  $\rm Cs_2$ , spin-orbit interactions become so significant that the  $2^3\Pi_g$  state is split into three component states. For  $\rm Rb_2$ , all three spin orbit components of the  $2^3\Pi_g$  state are produced in direct excitation, whereas for  $\rm Cs_2$ , most excitation wavelengths produce only one of the three spin-orbit components.

#### Introduction

Diffuse bands, especially of the alkali dimers, are interesting and important since they are thought to be primarily excimer-like triplet-triplet electronic transitions in which the lower triplet state is essentially repulsive. Because of inherent population inversions and relatively broad spectral ranges, they are potentially important continuously tunable laser sources. The alkali diffuse bands have been observed from the UV to the IR in absorption spectra, electric discharge excitations, and laser excitations. Moreover, Bahns and Stwalley have measured significant gain in the Na2 violet band, Dinev et al. have observed the triplet-triplet IR laser emission of Na2, and Heneghan, Chakravorty and Stwalley have measured significant gain in the K2 yellow band. Here, in order to understand the characteristics of the potential curves of the electronic states involved in the diffuse bands mentioned above, we have used direct dye laser excitations.

# Experimental

Three heat-pipe ovens (K, Rb, Cs) were used in this study. The dye laser (Coherent 599-21) was pumped by an argon ion laser at

<sup>\*</sup> Also Department of Chemistry, National Kaohsiung Teachers' College, Kaohsiung 80243, Taiwan, Republic of China

<sup>†</sup> AFRPL/LKCS/Stop 24, Edwards Air Force Base, Edwards, California 93512-5000

<sup>\*</sup> Also Department of Physics

514.5 nm. Four laser dyes, Rhodamine 560, 590 and 610, and LDS 698 (all from Exciton), were used. Their lasing spectral ranges are 540-600 nm, 570-650 nm, 601-675 nm and 688-708 nm, respectively. The former two dyes were used for K2, the latter two for Rb2 and Cs2, respectively. The dye laser (usually operated multimode) was tuned at intervals of 1 nm across the wavelength ranges of the diffuse bands. For each excitation wavelength, the fluorescence spectra were taken at selected pressures (typically a few torr), resolved using a Jarrell-Ash 8200 half-meter spectrometer, detected using an RCA 4832 photomultiplier with a PAR 134 electrometer, and recorded with a Linseis LS44 strip chart recorder.

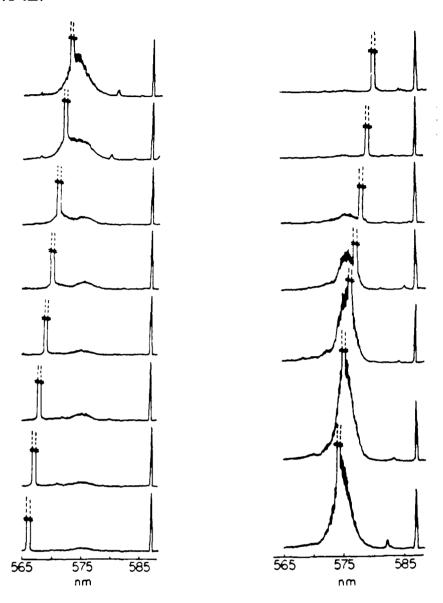
# K<sub>2</sub> Yellow Diffuse Band

A series of fluorescence spectra is shown in Figure 1 at a pressure of 2.9 torr. The observed fluorescences are obviously unstructured continua. They can be interpreted as follows. The K2 yellow diffuse band is presumably due to a triplet-triplet transition  $(2^3\Pi_g-1^3\Sigma_u^+)^5$  analogous to that observed for the Na<sub>2</sub> violet If so, one may observe unstructured bound-free continuum fluorescence following nonselective free-bound excitations since, according to recent ab initio calculations, the lowest triplet state  $1^{3}\Sigma_{u}^{+}$  of  $K_{2}$  has a very shallow well of depth 498 cm<sup>-1</sup> (which is approximately kT in this work), and one may expect most of the absorbing species in this triplet state are in free levels. Our observations in Figure 1 are indeed unstructured fluorescence continua and suggest that the  $1^3\Sigma_{\mathbf{u}}^+$  state is the lower electronic state involved. If the major relaxation processes of the upper electronic state bound levels are radiative, a measure of the spectrally integrated diffuse band fluorescence intensity versus excitation wavelength should resemble the absorption spectrum provided that the spectral response of the PMT detector in the range of interest is independent of wavelength. This is in fact the case if one compares our results to the reduced absorption coefficients of the same diffuse band from Johnson et al. 8 and Pichler et al. 9. This suggests that the relaxation processes from the upper electronic state bound levels are mainly back to the lower  $1^3\Sigma_{\mathbf{u}}^+$  state. One expects, that bound-bound transitions are also possible, although the well depth is only about kT. To look for this, a single mode dye laser was also used through the entire diffuse band range to obtain excitation spectra. There was no clear evidence that any bound-bound triplet emission is excited. The free-free fluorescence is expected to be negligible at these wavelengths. In summary, the above observations show that one is indeed dealing with bound-free fluorescence following free-bound excitation, which energetically corresponds to the  $2^{3}\Pi_{\sigma}$  -  $1^{3}\Sigma_{1}^{+}$  electronic transition.

## Rb2 Orange Diffuse Band

Similar diffuse band spectra were taken for Rb. One observes that these spectra are resolved into three peaks, located at 601.1 nm, 604.0 nm and 606.1 nm, respectively, unlike the single broad one

Figure 1.  $K_2$  spectrally resolved diffuse band fluorescence in the 564-587 nm range excited by dye lasers in the range 565-578 nm at 1 nm intervals. The reference line at the right of each spectrum is Kr at 587.1 nm.



for the  $K_2$  yellow diffuse band. It is well-known that spin-orbit interaction occurs in the multiplet electronic states with  $\Lambda \neq 0$  and its significance increases rapidly with increasing numbers of electrons. Thus for the heavy molecules, the  $2^3\Pi_\sigma$  state is expected to be split into three different states:  $2^3\Pi_{0g}$ ,  $2^3\Pi_{1g}$  and  $2^3\Pi_{2g}$ . These dye laser excitation studies show that the Rb2 orange diffuse band

can be interpreted in terms of the  $2^3\Pi_g$  -  $1^3\Sigma_u^+$  transition in which the upper state is split into three component states due to spin-orbit interaction  $^{10}$ .

## Cs2 near infrared diffuse band

Observed fluorescence spectra for  $Cs_2$  show diffuse band fluorescence, peaking at 718.9 nm, 712.9 nm and 707.5 nm. The separations between these three locations are larger than those of the Rb2 orange diffuse band and are consistent with a stronger spin-orbit interaction expected for  $Cs_2$ . Because of the stronger spin-orbit interaction, the three component upper electronic states can be excited quite independently.

## Summary

Dye laser direct excitation studies of the  $K_2$  yellow,  $Rb_2$  orange and  $Cs_2$  near infrared diffuse bands show at least semiquantitatively that (1) they originate from an electronic transition between an upper bound triplet state and a lower repulsive triplet state; (2) from the point of view of energetics, the upper bound state is very likely the  $2^3\Pi_g$  state which dissociates into a ns ground state atom and a (n-1)d excited atom; and (3) for the  $Rb_2$  orange and  $Cs_2$  near infrared diffuse bands, three different electronic transitions are involved because the  $2^3\Pi_g$  state is split into three separate components due to the stronger spin-orbit interactions. Agreement with previous experiments is good, as summarized in Table I.

Table I. Main Peak of the  $2^3\Pi_g$  -  $1^3\Sigma_u^+$  Diffuse Band of Alkali Metal Dimers.

$M_2$	hpeak(nm)		
	this work	others	
Li <sub>2</sub>	• •	458.512	
Na <sub>2</sub>	• -	436.51,13	
К2	575.0	574.513, 572.514, 575.010	
Rb <sub>2</sub>	606.1 604.0 601.1	605.4 <sup>10</sup> , 606.1 <sup>15</sup> 603.2 <sup>10</sup> 600.7 <sup>10</sup> , 600.8 <sup>15</sup>	
Cs <sub>2</sub>	718.9 712.9 707.5	718.510, 71811, 718.716 712.910, 71311, 712.716 705.410, 70711, 70616	

#### Acknowledgments

We would like to thank Drs. S. P. Heneghan and G. Pichler for helpful discussions and Dr. D. D. Konowalow for providing his ab initio results before publication. Supported by the Air Force Office of Scientific Research, the National Science Foundation and the Ministry of Education of the Republic of China.

#### References

- 1. J. P. Woerdman, Opt. Commun. 26, 216 (1978).
- J. T. Bahns and W. C. Stwalley, Appl. Phys. Lett. <u>44</u>, 826 (1984).
- 3. S. G. Dinev, I. G. Koproinkov and I. L. Stefanov, Opt. Commun. 52, 199 (1984).
- S. P. Heneghan, K. P. Chakravorty and W. C. Stwalley, private communication.
- G. Pichler, J. T. Bahns, K. M. Sando, W. C. Stwalley, D. D. Konowalow, L. Li, R. W. Field and W. Mueller, Chem. Phys. Letters, <u>129</u> 425 (1986).
- W. T. Luh, J. T. Bahns, K. M. Sando, W. C. Stwalley, S. P. Heneghan, G. Pichler and D. D. Konowalow, Chem. Phys. Letters 131, 335 (1986).
- 7. D. D. Konowalow, J. L. Fish, and C. Duda, private communication, March, 1984.
- 8. D. E. Johnson and J. G. Eden, J. Opt. Soc. Am. B 2, 721 (1985).
- D. Veza, S. Milosevic and G. Pichler, in K. Burnett, editor, <u>Spectral Line Shapes</u>, Volume 2 (de Gruyter, New York, 1983), p. 679.
- 10. G. Pichler, S. Milosevic, D. Veza and R. Beuc, J. Phys. B <u>16</u>, 4619 (1983).
- P. Cavaliere, G. Ferrante and L. L. Cascio, J. Chem. Phys <u>62</u>, 4753 (1975).
- 12. J. T. Bahns, W. C. Stwalley and G. Pichler, J. Chem. Phys., in press.
- 13. Cz. Radzewicz, P. Kowalczyk and J. Krasinski, Opt. Comm. 44, 139 (1983).
- 14. M. M. Rebbeck and J. M. Vaughan, J. Phys. B 4, 258 (1971).
- J. M. Brom, Jr. and H. P. Broida, J. Chem. Phys. <u>61</u>, 982 (1974).
- 16. W. Finkelnburg and O. Th. Hahn, Phys. Z. 39, 98 (1938).

# EMED A